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Passivation of Anodic Reactions

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ABSTRACT

Carl Wagner has given the following phenomenological definition of passivity in Corrosion Science 5:751 (1965). "A metal may be called passive when the amount of metal consumed by a chemical or electrochemical reaction at a given time is significantly less under conditions corresponding to a higher affinity of the reaction (i.e., a greater decrease in free energy) than under conditions corresponding to a lower affinity." Extending the Wagner definition of passivity to anodic reactions of chemical species on inert electrodes, passivation of a Pt electrode for the hydrogen oxidation reaction can be explained as being caused by small amounts (fraction of a monolayer) of adsorbed anions. Anion adsorption can effectively reduce the active electrode area, but the major passivation effect is the poisoning of catalytic sites, which retard the catalytic reaction so that in most of the region where passivation occurs the reaction rate is controlled by the increased free energy of activation with increased potential. The change in sign from positive to negative of the kinetic relation $dE/d(\log i)$ can be explained as being caused by adsorption of a small number of anions and is limited when the active sites are essentially saturated. Adsorbed oxygen atoms in addition to sulfate ions can have a strong effect on the catalytic activity of Pt for the hydrogen oxidation reaction. This concept may be extended to other retarded anodic reactions and to the passivation of iron in particular.

PROBLEM STATUS

This is an interim report on one phase of the problem; work on this and other phases of the problem is continuing.

AUTHORIZATION

NRL Problems C05-06 and M04-08
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PASSIVATION OF ANODIC REACTIONS

INTRODUCTION

Wagner (1) has given the following phenomenological definition of passivity: "A metal may be called passive when the amount of metal consumed by a chemical or electrochemical reaction at a given time is significantly less under conditions corresponding to a higher affinity of the reaction (i.e., a greater decrease in free energy) than under conditions corresponding to a lower affinity." An electrochemical example given by Wagner is that the steady-state rate of anodic dissolution of a metal in a given environment is lower at a more noble single electrode potential than at a less noble potential.

This definition of passivity can be extended to include reactions other than the oxidation of metals (2). Oxidation reactions of chemical species at an inert metal surface also can decrease under conditions corresponding to a higher affinity of the reaction. A well-known example of this is the oxidation of hydrogen on a Pt electrode in sulfuric acid solution under an atmosphere of hydrogen gas (3). Under potentiostatic steady-state conditions (Fig. 1) as the overvoltage is increased in a noble direction the rate of hydrogen oxidation increases until a potential of 0.05 v (vs NHE) is reached. At increasingly noble potentials the current density (reaction rate) remains constant ($i = 2 \text{ ma/cm}^2$, true area) up to a potential of about 0.7 v. At potentials greater than 0.7 v the rate of oxidation of hydrogen decreases until a potential of 1.2 v is reached. We (3) concluded that the decrease in the rate of hydrogen oxidation in this range was due to the adsorption of sulfate ion, which caused an increase in the free energy of activation of the anodic hydrogen reaction. As the potential was changed from 0.7 to 1.2 v, the increased coverage of the Pt electrode with the sulfate ion further retarded the reaction.

It was shown (3) that passivation of the hydrogen oxidation reaction in the potential range from 0.7 to 1.2 v could not be due to the formation of oxygen species on the electrode surface. This is because the rate of the chemical reaction of such oxygen species on Pt with hydrogen would be orders of magnitude faster than their rate of formation. In addition, hydrogen oxidation is much faster than water oxidation. Hence, from 0.7 to 1.2 v the existence of adsorbed oxygen atoms, other oxygen species, or Pt oxides which may be found in this potential range would be very short-lived and the accumulation of such species on the surface could not occur.

In passing, an explanation should be given as to why water will be rapidly oxidized to oxygen atoms which deposit on the Pt surface with a high current density anodic pulse starting at a potential of about 0.5 v (6), whereas, at steady-state potentiostatic conditions, the rate of water oxidation is so slow (7) in the potential range from 0.7 to 1.2 v and the rate of hydrogen oxidation and reduction of oxygen atoms with hydrogen is so fast (3) that oxygen atoms cannot exist on the surface in this potential range. A high current density anodic pulse only sees the hydrogen and water adsorbed on the Pt surface. These surface species are all very rapidly oxidized with high current density anodic pulses. Thus, water, or water fragments, which is strongly adsorbed on the Pt surface can be rapidly oxidized with such anodic pulses.

In short, the reactivity of species initially associated with a surface before a rapid current or voltage perturbation is applied may be quite different from the steady-state reactivity of like species or their parents coming to the surface from the solution.

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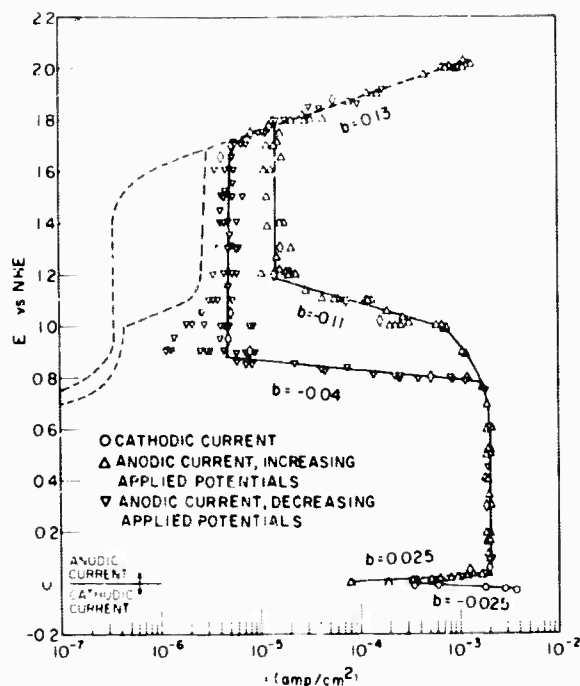


Fig. 1 - Steady-state potentiostatic current density vs potential relation on Pt in hydrogen-saturated 1M H_2SO_4 . The H_2 flow rate is greater than 1000 ml/min. The broken line is the relation in He-saturated solution (7), where the hysteresis line to the right is for increasing applied potentials and the hysteresis line to the left is for decreasing applied potentials. (From Ref. 3.)

Another example of this is the very fast reaction of chemisorbed organic species under high current density pulses - organic species which react very slowly under steady-state conditions.

For the overall reaction,



Following Parson's (4) analysis, and since at high anodic potentials the amount of coverage of the electrode with adsorbed H atoms will approach zero, the Langmuir adsorption isotherm is approximated, we can express the reaction rate as

$$i = k P_{\text{H}_2} \theta^n \exp(-\Delta G^\circ/RT) \exp(\alpha F/nRT), * \quad (2)$$

*This equation represents the various kinetic factors which may influence the measured current density. In fact, since in the potential region from 0.04 to 0.7 v, current density is independent of potential, and if the rate-controlling mechanism remained the same above 0.7 v, the only effect of potential may be on anion adsorption. Of importance is that because of the changes on the electrode surface induced by potential changes in the passivating region, the reaction rate is dependent primarily on the effective electrode area and a nominal free energy of activation required to oxidize hydrogen under the given surface states.

where k is a constant, P_{H_2} is the partial pressure of hydrogen, θ is the effective fraction of sites on the Pt surface where oxidation can occur, n is the reaction order, ΔG° is the standard free energy of activation for the reaction when $\phi = 0$, ϕ is the inner potential difference between metal and solution, α is the transfer coefficient, and F , R , and T are the faraday, gas constant, and Kelvin temperature, respectively. Under given conditions of concentration of reactants one would normally expect the exponential term containing the potential to determine the reaction rate i . As the applied potential is increased, the reaction rate will increase until a limiting condition is reached where the reaction rate will remain independent of increased potential. If under certain potential conditions, the reaction, or reaction mechanism, or the rate-controlling step of the overall reaction changes, then ΔG° can change and therefore affect the current density. However, such a change is normally reflected in a change in the Tafel b ($= dE/d(\log i)$) slope rather than a retardation of the reaction rate. This is because the controlling free energy of activation of an anodic reaction is decreased as the potential is made more noble. However, under passivation, $dE/d(\log i)$ changes from a positive to a negative value.

EXPERIMENTAL DATA

Figure 2 shows the number of coulombs of charge required to saturate a potentiostated Pt bead electrode with adsorbed oxygen atoms. The experiment was carried out in 1 M H_2SO_4 saturated with hydrogen at 1 atm. (The experimental conditions were the same as previously reported (3).) The q_o value is the number of $\mu\text{coul}/\text{cm}^2$ of charge required to fill the available Pt sites with adsorbed oxygen atoms. This was determined by potentiostating the Pt electrode at a given potential, then very rapidly ($1 \mu\text{sec}$) switching from potentiostatic control to a high current density anodic charging pulse (see Ref. 5 for instrumentation).

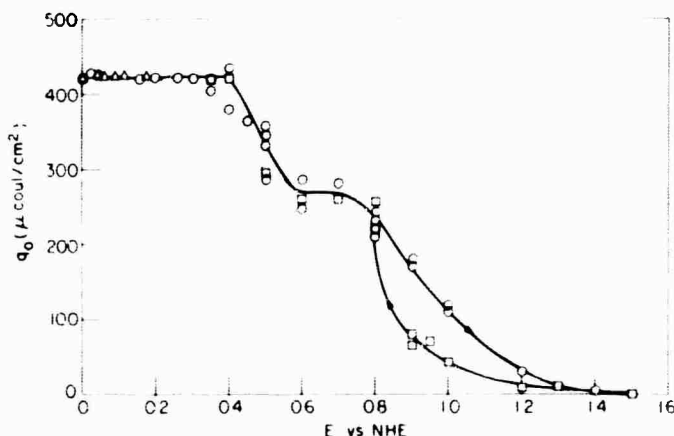


Fig. 2 - Amount of oxygen formed on a potentiostatic Pt electrode in a 1M H_2SO_4 solution and under 1 atm of hydrogen gas. The anodic charging current density pulse is equal to $1.8 \text{ amp}/\text{cm}^2$.

Figure 2 shows that up to potentials of about 0.4 v the number of free sites on the Pt surface which can adsorb oxygen atoms remains constant and is equivalent to about one monolayer. At potentials more noble than 0.4 v the number of sites decreases and remains essentially constant at about 3/4 of the monolayer value between 0.6 and 0.7 v. At potentials above 0.7 v the number of available sites drops and is equal to zero at about 1.5 v. The decrease in free Pt sites apparently occurs in two phases. Whatever is causing the drop in available sites in the potential region between 0.4 and 0.6 v does not affect

the rate of hydrogen oxidation. However, at potentials beyond 0.7 v the rate of hydrogen oxidation decreases. The cause of the hysteresis shown in both Figs. 1 and 2 is due to dermasorption of oxygen atoms at higher potentials (3). This dermasorbed oxygen decreases the number of surface sites which can adsorb oxygen (Fig. 2).

The data in Figs. 1 and 2 demonstrate that the onset of passivity is accompanied by a decrease in the number of sites available for oxygen-atom adsorption with an anodic charging pulse. At 1.2 v, where a limiting current density is reached, the number of such sites is small. Since it was previously shown (3) that steady-state passivation due to oxygen species or oxide formation in a hydrogen-saturated sulfuric acid solution was not feasible, those sites which are unavailable for oxygen-atom adsorption with a high current charging pulse are considered occupied by sulfate ions under steady-state potentiostatic conditions.

DISCUSSION

In the light of the Wagner definition of passivity and Eq. (2), we can conclude that two possible factors cause passivation of the hydrogen oxidation reaction. One is a decrease in the number of available active sites, and the other is an increase in the free energy of activation for each increment of potential increase. The data in Fig. 2 indicate a drop in the number of sites available for oxygen-atom adsorption between 0.4 and 0.6 v; however, there is no accompanying retardation of the hydrogen oxidation rate in this potential range (Fig. 1). This means that active hydrogen oxidation sites are not affected in this potential range. The potential-increasing arm in Fig. 1 shows a relatively small retardation of the hydrogen oxidation rate in the potential range from 0.7 to 1.0 v, followed by a sharp exponential decrease ($b = -0.11$) from 1.0 to 1.2 v. The potential-decreasing arm of the data in Fig. 1 shows in the potential range from 0.9 to 0.75 v a much higher dependence of reaction rate on potential ($b = -0.04$).

For the rising potential range from 0.7 to 1.0 v the fraction of available sites for oxygen-atom adsorption (Fig. 2) changes from about 0.6 to 0.25. In this same potential range Fig. 1 (rising potentials) shows a decrease in hydrogen oxidation rate from $2 \cdot 10^{-3}$ to $7 \cdot 10^{-4}$ amp/cm². If we consider the change in available oxygen sites as a change in available reaction sites for hydrogen oxidation, it will amount to a reduction in area of about 0.4; the accompanying reduction in reaction rate is about 0.35. In terms of Eq. (2), this amounts to $n \approx 1$ and satisfactorily explains the reduction in hydrogen oxidation rate when θ changes.

The changes in reaction rate from 1.0 to 1.2 v on the increasing potential arm (Fig. 1) correspond to a 0.2 reduction in sites available for oxygen deposition with a decrease in reaction rate by a factor of 50. The decreasing potential arm from 0.9 to 0.75 v showed a 0.4 increase in sites with about a 1000-time increase in reaction rate. Neither the passivation in the linear log ($b = -0.11$) increasing potential arm nor the activation in the linear log ($b = -0.04$) decreasing potential arm can be attributed to the θ term in Eq. (2). We can therefore conclude that the passivation in these potential ranges must be due to a condition where each small increment of potential causes a significant change in the free energy of activation ΔG° for the hydrogen oxidation reaction. The exponential term containing ΔG° must override the exponential potential term.

The number of catalytically active sites on a clean Pt electrode is very small (as is evident from the fact that the rate of the hydrogen reaction on Pt is very sensitive to trace amounts of impurities). It appears that on the increasing potential arm of Fig. 1, up to a potential of 1.0 v, adsorption of the sulfate ion merely blocks part of the catalytically active sites. At potentials above 1.0 v, however, the sulfate ion must be so strongly adsorbed that it acts like a catalytic poison and causes a large increase in the free energy of activation for the hydrogen oxidation reaction. On the decreasing potential arm shown

in Fig. 1 and in the potential range from 0.9 to 0.75 v ($b = -0.04$), the Pt contains a small amount of dermasorbed oxygen (3,7). This trace of dermasorbed oxygen evidently has an important effect on the value of the free energy of activation. Dermasorbed oxygen in combination with adsorbed sulfate ion therefore acts as a very strong catalytic poison.

Uhlig (8) has for some time offered as an explanation of passivity the combined effects of chemisorbed oxygen species and resultant decreases in catalytic activity. Our work on the anodic oxidation of hydrogen on Pt confirms Uhlig's hypothesis and extends the possible catalytic poisons to anion adsorption.

CONCLUSIONS

The data on the anodic oxidation of hydrogen on Pt evaluated in terms of the extended Wagner definition of passivity clearly show that passivation can be caused by small increases (a fraction of a monolayer) in the amount of anion adsorbed and that the passivation process is limited when the Pt surface is essentially saturated with these adsorbed anions. Small amounts of sorbed species may cause large changes in the free energy of activation for the reaction and lead to the conclusion that since the role played by active Pt sites is that of a catalyst for the hydrogen reaction, the adsorption of anions (and dermasorption of oxygen atoms) can effect a poisoning of active sites and a subsequent rate-controlling increase in the free energy of activation for the reaction.

One can extend this analysis to the passivation of iron. Here the dissolution of iron can be considered to involve a catalytic step, which may be retarded by chemisorption of poisons at a given potential. The influence of oxygen species associated with the iron could also have a large effect.

The primary purpose of this report is to demonstrate that the Wagner definition of passivation naturally leads to the conclusion that passivity, so defined, is initiated by adsorption of small amounts (a fraction of a monolayer) of species which can either reduce the active surface area or act as catalytic poisons. The primary effect for large passivation effects appears to be the adsorption of catalytic poisons which cause large increases in the free energy of activation of the reaction. The passivation process itself ($b = -dE/d(\log i)$) is limited by saturation of the active sites with such poisons.

This, of course, does not mean that there are not other reasons and processes for slow oxidation reactions under other conditions. The value of the extended Wagner definition is that it leads to a reasonable explanation of an unusual kinetic occurrence - the reversal of the $dE/d(\log i)$ slope.

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